P1 989498

REC'D 16 APR 2003
WIPO PCT

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

April 08, 2003

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: *60/361,563*
FILING DATE: *March 04, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/06455*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

P. SWAIN
Certifying Officer

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

03-05-02

APPROV

Please type a plus sign (+) inside this box → [+]

PTO/SB/16 (8-00)
Approved for use through10/31/2002. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Chad	Buckley	Perkinston, Mississippi

☐ *Additional inventors are being named on the ____ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (280 characters max)

Improved Polyvinyl Alcohol Water-Soluble Film

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☐ Customer Number [ ] → *Place Customer Number Bar Code Label here*

OR *Type Customer Number here*

☒ Firm or Individual Name	Robert M. Bowick				
Address	1900 West Loop South				
Address	Suite 1800				
City	Houston	State	Texas	ZIP	77027
Country	U.S.A.	Telephone	(713) 355-4200	Fax	(713) 355-9689

ENCLOSED APPLICATION PARTS *(check all that apply)*

☒ Specification *Number of Pages* [ ]
☐ CD(s), Number [ ]
☐ Drawing(s) *Number of Sheets* [ ]
☐ Other (specify) [ ]
☐ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT *(check one)*

☒ Applicant claims small entity status. See 37 CFR 1.27.
☒ A check or money order is enclosed to cover the filing fees
☒ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 13-2166
☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE AMOUNT ($): $80.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.
☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE

Date 3/4/02

TYPED or PRINTED NAME Robert M. Bowick

REGISTRATION NO. (*if appropriate*) 46,569

Docket Number: Buckley-001

TELEPHONE (713) 355-4200

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C.

P18SMALL/REV05

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): **Chad Buckley**			Docket No. **Buckley-001**
Serial No.	Filing Date **4 March 2002**	Examiner	Group Art Unit

Invention: **Improved Polyvinyl Alcohol Water-Soluble Film**

I hereby certify that the following correspondence:

Provisional Application cover sheet; and all documents references therein.

(Identify type of correspondence)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on

4 March 2002
(Date)

Matt Robinson
(Typed or Printed Name of Person Mailing Correspondence)

(Signature of Person Mailing Correspondence)

EL 921419852 US
("Express Mail" Mailing Label Number)

Note: Each paper must have its own certificate of mailing.

P06A/REV02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

- Provisional Patent Specification -

Inventor:
CHAD BUCKLEY
Invention:
IMPROVED POLYVINYL ALCOHOL WATER-SOLUBLE FILM

Prepared by:

The Matthews Firm
1900 West Loop South Suite 1800
Houston, Texas 77027

Telephone: 713/355-4200
FAX: 713/355-9689

(Docket No.: Buckley-001)
[Printed: March 4, 2002]

IMPROVED POLYVINYL ALCOHOL WATER-SOLUBLE FILM

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to polyvinyl alcohol (PVOH) water-soluble films, and particularly to water-soluble films that are designed with a non-migratory plasticizer system for increasing the long term use of the film.

2. BACKGROUND OF THE INVENTION

Water-soluble films are commonly used in applications for single dose packages. These water soluble packages provide benefits including but not limited to providing precise dosing of materials contained within the packaging, providing an environmentally safe disposal of the packaging, convenient handling of the package's contents and user safety in that the packaging avoids the need for the user to open and expose the contents of the packaging. Such packaging is often utilized for containing highly reactive materials including pesticides, fertilizers and more recently soaps and detergents.

Caustic or potentially hazardous materials such as detergents, soaps, plant protection agents, dyes for the textile industry, concrete additives, and fertilizers are typically packaged in dispensers, such as high density polyethylene bottles, or other containers. After the chemical contents of the container have been spent, the empty dispenser or container must be disposed of in an environmentally safe way. This can be technically difficult and expensive.

Water-soluble films are useful in many applications in addressing these problems. When a product is needed, the package is immersed in water or some aqueous based medium to dissolve the contents of the package in the aqueous medium while additionally dissolving the packaging material itself. Such uses offer an environmentally attractive alternative to containers, which do not dissolve, and must therefore be disposed of after use.

This invention relates to poly-vinyl alcohol (PVOH) homo and co-polymer based films and the incorporation of non-migratory plasticizer systems to retard and summarily halt the leeching of plasticizers. Plasticizers are incorporated into PVOH films to increase the flexibility of the film. Commercially available PVOH films are produced via melt extrusion or solution casting methods. In both processes a highly crystalline PVOH (12-18% crystallinity for 88% hydrolyzed PVOH and 30-50% crystallinity for 99+% hydrolyzed PVOH) is mixed with a plasticizer to reduce the total amount of crystallinity of the finished, water-soluble film. In most cases, measurement by Differential Scanning Calorimetery (DSC) indicates that highly plasticized PVOH films have a total heat capacity of 4.65 joules/gram or approximately 1.5% crystalline in nature. The percent crystallinity is dividing the heat capacity of the film by the heat capacity of a perfect crystal (277.4 joules/gram). The reduction of crystallinity by the addition of a plasticizer has proven to be effective in the formation of flexible films with excellent odor barriers and superior strength properties. However, the introduction of plasticizers into the PVOH system is a non-covalent reaction and such plastification is only a temporary solution. Over time, the film begins to revert back to its highly ordered state and begins to crystallize (the gradual reduction in entropy driving plasticizer out of the system). To

retard or halt this decrease in amorphous regions of the film, the PVA/plasticizer system must be kept intact.

3. DESCRIPTION OF THE PRIOR ART

The use of polyvinyl alcohol (PVOH) water-soluble film is known in the prior art. More specifically, these water-soluble films are most commonly used in applications for single dose packages, notwithstanding the myriad of uses encompassed by the crowded prior art which have been developed for the fulfillment of countless objectives and requirements. Known prior water-soluble packaging include U.S. Patent Nos. 5,529,888; 4,544,693; 4,528,360; 5,827,586; 6,166,117; Re.34,988; 5,051,222; 4,557,852; 3,198,740; 4,176,074; 4,973,416; 5,429,874; 6,133,214; 5,806,284; 5,827,586; 4,765,916; 6,071,618.

These prior art films initially exhibit great water-solubility and flexibility. However, long-term aging studies have indicated that these films harden, become brittle and lose solubility. U.S. Patent No. 6,303,553 discloses a water-soluble package containing a powdered automatic dishwashing composition that can be added directly to an automatic dishwasher. Quantitative analysis has conclusively demonstrated that the polyvinyl alcohol (PVOH) films disclosed therein tend to become harden, brittle and less soluble over time caused by the migration of plasticizers out of the "system", thus increasing the overall crystalline nature of the film.

Conventionally, solution-cast PVOH films are considered unstable and difficult to formulate to minimize product interaction. This is due in part because the process of solution-casting PVOH requires the addition of water, plasticizers, caustic liquids, and

surfactants to the film system. This type of complex film system allows for the cross migration of opportunistic chemicals, which commonly causes premature failure in the film. Additionally, these types of films tend to dry out and become brittle over time reflecting their dependence on water as a plasticizer.

In general, extruded films have no such product interactions because they are produced via a compounding of PVOH into a thermoplastic, contain no surfactants or caustic materials and do not require the use of water to plasticize the package. However, the ability of extruded films to retain plasticizers meets a similar fate to that of solution-cast films due to the formation of crystals in the extruded film that leeches plasticizers over time. The formulations of the present invention counteract the adverse effects of plasticizer migration.

U.S. Pat. No. 4,973,416 discloses the packaging of an aqueous liquid laundry detergent in a package of water-soluble film-forming material. Specifically the patent teaches the use of a liquid laundry detergent comprising 10%-24% by weight of water combined with a neutralization system so that the detergent solution to prevent a reaction with a water-soluble film.

U.S. Pat. No 5,429,874 discloses the use of salts in PVOH films to increase the solubility of non PVOH based polymers, which were not normally soluble at room temperature in water. However, this patent did not contemplate the use of such salts to maintain the plasticizer systems in a PVOH film.

4. DEFINITIONS

"Water soluble" as used herein refers to a film structure, which is preferably totally water soluble or water-dispersible. However, films which are substantially water soluble but have relatively minor amounts of a material in the film structure which is not water soluble; films with materials which are water soluble only at relatively high water temperatures or only under limited pH conditions; and films which include a relatively thin layer of water insoluble material, are all included in the term "water soluble". "Film" is used herein to mean a film, web, or other packaging material of one or more layers, made by e.g. extrusion, co-extrusion, lamination (extrusion, thermal, or co-reactant solvent-based or water based adhesive system), coating, or other processes. Films are known from the prior art and emanate for example from the group of (acetalized) polyvinyl alcohol, polyvinyl pyrrolidone, poly-ethylene oxide, gelatin and mixtures thereof. Water-soluble film which forms a package has a thickness of 1 to 150 microns, preferably 2 to 100 microns, more preferably 5 to 75 microns and most preferably 10 to 50 microns.

"Caustic" is used herein to mean a chemical or mixture of chemicals with a pH of 7.0 or higher, i.e. alkaline. "PVOH" is used herein to polyvinyl alcohol including polyvinyl acetate compounds with levels of hydrolysis disclosed herein. Polyvinyl alcohols are polymers with the following general structure:

[-CH2-CH(OH)-]n

which also contain small amounts of structural units of the following type:

[-CH2-CH(OH)-CH(OH)-CH2]

Since the corresponding monomer, vinyl alcohol, is not stable in free form, polyvinyl alcohols are produced via polymer-analog reactions by hydrolysis and-on an industrial scale-above all by alkali-catalyzed transesterification of polyvinyl acetates with alcohols (preferably methanol) in solution. PVOHs containing a predetermined residual percentage of acetate groups can also be obtained by these industrial processes.

Commercially available PVOHs (for example Mowiol(r) types, products of Clariant) are marketed as white-yellowish powders or granules with degrees of polymerization of ca. 500 to 2,500 (corresponding to number average molecular weights of ca. 20,000 to 100,000) and have different degrees of hydrolysis of 98-99 or 87-89 mole-%. Accordingly, they are partly saponified polyvinyl acetates with a residual content of acetyl groups of ca. 1-2 or 11-13 mole-%.

"Polymer" is used herein to mean macromolecule made up of a plurality of chemical sub-units (monomers). The monomers may be identical or chemically similar, or may be of several different types. Unless a more specific term is used, "polymer" will be taken to include hereto- and homo- polymers, and random, alternating, block and graft polymers.

5. DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides for polyvinyl alcohol (PVOH) which incorporates a non-migratory plasticizer system. For the purpose of this invention, the "system" comprises a PVOH film comprised of a blend of a high molecular weight plasticizer, a low molecular weight plasticizer and either a mineral or salt nucleating agent. As used herein, low molecular weight plasticizer includes plasticizers with molecular weights less

than 200 amu, while high molecular weight plasticizers includes plasticizers with molecular weights grater than 500 amu.

The present invention includes a film comprising of, a PVOH and by weight, 0.1% - 20% mineral and/or salt nucleating agent and 5-25% plasticizer, excluding water. Specifically, the PVOH component of the film is preferably 60-94.4% by weight, the PVOH being 50 - 99+ mole percent hydrolyzed with a degree of polymerization of 500-2500. Higher molecular weight polymers increase the physical properties of the corresponding PVOH films as well as reduce their interaction with humidity. Ideally this plasticizer/PVOH non-migratory system would have a degree of polymerization of 800 for a base PVOH that is 87% hydrolyzed.

The mineral or salt nucleating agent can be any substantially inert powder, including: diatomaceous earth, talc, sodium sulfate, magnesium/aluminum silicates, calcium carbonate, silicone oxide, any of which having a particle size from 0.1 - 25 microns. This specific particle size and amount of nucleating agent, when properly dispersed, produces a highly ionic network throughout the film. This network tends to pool the plasticizers, and keeps the total entropy of the film system from decreasing. The film can be melt extruded, comprised of one or more layers via co-extrusion, lamination or the application of surface coatings. As a possible alternative, a solution-cast film might also be attainable, employing the present invention.

Preferred salt nucleating agents are alkali or alkaline earth salts such as sodium carbonate (Na2CO3); sodium sulfate (Na2SO4); sodium chloride (NaCl); potassium carbonate (K2CO3); potassium sulfate (K2SO4); and potassium chloride (KCL). One or

more of these water-soluble salts can be included in the water-soluble film or the invention. The salt can be present in any suitable concentration in a given layer. Optimal concentrations will be governed to some extent by the nature of the salt, the nature of the base resin, the specific use of the film, processing and packaging equipment, and other factors.

The plasticizer "system" can be one of or a combination of conventional plasticizers, including propylene glycol, ethylene glycol, polyethylene glycol, 1,2,3 propanetriol, mannitol, pentaerythritol, and trimethylolpropane. A combination of polyethylene glycol, propylene glycol and 1,2,3 propanetriol is a preferred plasticizer system. The invention will be better understood by reference to the following detailed description. The incorporation of high molecular weight plasticizers reduces large crystalline regions within the film while low molecular weight plasticizers reduces the small crystalline regions.

The blend of both high and low molecular weight plasticizer as well as the nucleating agent significantly reduces the leeching of the plasticizer system in the film. Prior art describes a process in which glycerin mono oleate (GMO) is required in the compounding step to act as a dispersing agent for a dual plasticizer system containing glycerin and polyethylene glycol. The GMO would be utilized in a high-speed mixer to properly disperse the plasticizers prior to their introduction to a compounding extruder. This present invention uses a mineral or salt nucleating agent to effectively disperse the plasticizers though out the thermo plastic during the compounding process, thus reducing the number of the steps required producing a thermo plastic PVOH compound.

The present invention provides for polyvinyl alcohol (PVOH) compositions that can be prepared by conventional, solution mixing or melt extrusion processing methods and incorporates a non-migratory plasticizer system. With the compositions of the present invention, a non-migratory PVOH/plasticizer film system incorporating mineral and/or salt nucleating agents to increase the long term use of the film.

After addition of the nucleating agent during the compounding step, the film can be melt extruded, comprising one or more layers via co-extrusion, lamination of the application of surface coatings. As a possible alternative, a solution-cast film might also be attainable employing the compositions of the present invention. The plasticizer "system" can be a combination of conventional plasticizers, including propylene glycol, ethylene glycol, polyethylene glycol, 1,2,3 propanetriol, mannitol, pentaerythritol, and trimethylolpropane.

For the production of a film of the present invention, the following commercially available products are readily available: 88% hydrolyzed PVOH is provided by Clariant grade Mowoil 8-88, with a number average molecular weight of 67,000 and a sodium acetate level of 1500 ppm or less. A virtually identical PVOH with similar molecular weight distribution as Mowoil 8-88 is GL05 provided by Nippon Goeshi. 98% hydrolyzed PVOH is also provided by Clariant grade Mowiol 6-98, with a number average molecular weight of 47,000 and a sodium acetate concentration of 1500 ppm or less. Kuraray provides hydrolyzed PVOH 73% with a grade Poval 505c, which has a number average molecular weight of 28,000 and a sodium acetate level of less than 500 ppm. 1,2,3-propanetriol is provided for and commercially available from Proctor and Gamble under the trade name Moon Glycerin USP. Polyethylene glycol with a degree of

polymerization of 400 as well as propylene glycol is made available from Dow Chemical. Chlorite and other magnesium/aluminum/ferrous silicates are also available from Luzenac America. The ideal particle size for the film of the present invention is between 1 - 1.7 microns.

The preferred film will be produced in a multi layer structure. The outer layers of the film would comprise a PVOH base polymer with a degree of polymerization of 500-2500 and having a total sodium acetate level of less than 1500 ppm. This layer would have a degree of hydrolysis of 50-90% and would be designed to give wet-ability and rapid dissolution to the film structure. This portion of the film would be plasticized with a high molecular weight plasticizer such as polyethylene glycol as to reduce the chances of producing a harmful smoke during the manufacturing of the film.

Film systems containing a low molecular plasticizer such as glycerin produce smoke for the volatilization of plasticizer just below the frost line of the bubble in a blown film manufacturing process. These structures are hard to consistently reproduce since the exact amount of plasticizer in the film varies form lot to lot due to the off gassing of low molecular weight organics. This invention details a method of producing a multi-layer film which, is essentially smoke free during the manufacturing process. This method allows for the incorporation of low molecular weight plasticizers into the inner layer of the film, which provides increased flexibility and solubility as well as to give the desired physical properties.

The main composition of the inner layers would be produce from a 50-90% hydrolyzed PVOH with a degree of polymerization of 500-2500. The plasticizer "system"

can be one of or a combination of conventional plasticizers, including propylene glycol, ethylene glycol, polyethylene glycol, 1,2,3 propanetriol, mannitol, pentaerythritol, and trimethylolpropane. A combination of polyethylene glycol, propylene glycol and 1,2,3 propanetriol is a preferred plasticizer with the addition of 0.5-20% mineral or salt nucleating agent with a particle size distribution of 0.1-25 microns

The invention may be further understood by reference to the examples identified below. Numerous tests have been performed on the various examples of the PVOH films. Optimizing the PVOH films has been a common goal of all the tests. The results of some of the tests run for enhancing the qualities of the PVOH films follow:

Example 1 "Three layer film with three extruders"

Layer A of Film Structure, Extruder 1

20% of Film Structure

Compound	% by weight
Mowiol 8-88	74
Polyethylene Glycol 400	25
Talc	1

Layer B of Film Structure, Extruder 2

60% of Film Structure

Compound	% by weight
Mowiol 8-88	80
1,2, 3 Propanetriol	10
Propylene Glycol	5
Polyethylene Glycol 400	3
Talc	2

Layer C of Film Structure, Extruder 3

20% of Film Structure

Compound	% by weight
Poval 505C	80
1,2,3 Propanetriol	16
Polyethylene Glycol 400	4
Talc	2

Having thus described the invention with particular reference to the preferred forms thereof it will be obvious that various changes and modifications may be made therein without departing from the spirit and scope of the invention as defined in the appended claims.

CLAIMS

What is claimed is:

A water-soluble, polymeric film comprising:

Polyvinyl alcohol, a low molecular weight plasticizer, a high molecular weight plasticizer; and a mineral or salt nucleating agent.

A water-soluble polymeric film in which GMO is not required in the formulation as a dispersing agent as an initial step before compounding the raw materials into a melt processable thermo plastic.

Where the film is a multi layer structure and is produced with the incorporation of low molecular weight plasticizers in such a manner as to not volatilize said plasticizers and produce smoke during the manufacturing process.

Where a water-soluble polymeric film utilizes a mineral or salt nucleating agent to effectively disperse and lock in the plasticizers within the film matrix.

ABSTRACT

This invention relates to improved water-soluble polymeric materials, and particularly to water-soluble films designed with a non-migratory plasticizer system for increasing the long-term use of the film. Specifically, the invention comprises a film comprising a blend of polyvinyl alcohol, a low molecular weight plasticizer, a high molecular weight plasticizer and a water-soluble or water-dispersible salt or mineral nucleating agent including any material which is water soluble, or substantially so, and capable of being incorporated into the film structure, preferable materials are salts or minerals. More particularly, the present invention relates to a system and method including providing a dissolvable film for packaging individually sealed dosages of materials.